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Dedicated to V. F. Mironov on His 60th Anniversary

Synthesis and Inner-Sphere Hydrophosphorylation of (η^1-*N*)-*N*-Benzyl-*N*-(1,3-dimethylbut-2-enylidene)amine-(dicarbonyl)(1,3,5-triorganyl-1,3,5-triazacyclohexane) molybdenum(0) and -tungsten(0)

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Abstract—Complexes of group VIb metals (Mo and W) has been prepared with *N*-benzyl-(3-methylbut-2-enylidene)amine, where the latter is coordinated with the dicarbonyl(1,3,5-triorganyl-1,3,5-triazacyclohexane)-metal(0) fragment exclusively through the lone electron pair of the imine nitrogen atom. The reactions of the synthesized metal complexes with diethyl phosphite in various conditions always involved the addition of the phosphite across the C=N bond to form, depending on the conditions, aminophosphonates or their inner-sphere rearrangement products amidophosphates. Both organophosphorus compounds remain in the coordination sphere of the transition metal complex.

Keywords: conjugated imines, inner-sphere hydrophosphorylation, 1,3,5-triorganyl-1,3,5-triazacyclohexanes, group VIb metals, aminophosphonate, amidophosphate

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Conjugated imines, compounds where the C=N bond is conjugated with the C=C bond, have long been widely used in organic and organometallic synthesis [1]. The results of our previous systematic research on the inner-sphere hydrophosphorylation of unsaturated heterodiene ligands [2–8] show that the synthetic result of the reactions is strongly affected both by the structure of the inner-sphere unsaturated molecule that reacts with the hydrophosphorylating agent and by the ligands coordinated with the transition metal and not involved in the hydrophosphorylation reaction. For example, the preparative isolation and study of the phosphaorganometallic products of the regioselective hydrophosphorylation of carbonyl metal complexes is complicated by the reversibility of the phosphorylation reaction and the tendency of the products to disproportionation [4, 5]. The problems associated with the stability of the functionalized complexes and phosphaorganometallic compounds derived from them can be solved using a properly selected assistant ligand, the main function of which should be preventing the disproportionation of the complex due to chelate binding to the metal center. Obviously, the assistant ligand should be insensitive to the functionalizing reagents.

We recently reported the inner-sphere hydrophosphorylation of α-enones in complexes stabilized by tridentate assistant ligands, specifically 1,3,5-triorganyl-1,3,5-triazacyclohexanes (triazinanes) [7] and tris(1*H*-pyrrol-2-yl)amine [9], as well as the bidentate *o*-phenanthroline [10]. At the same time, the reactions of enamines with hydrophosphoryl compounds in the coordination sphere of group VIb metals were studied only for the readily disproportionating complexes with carbonyl ligands [5], as well as for an organometallic compound stabilized with tris(1*H*-pyrrol-2-yl)amine [9].

For a deeper understanding of the features of the inner-sphere hydrophosphorylation of conjugated amines and the effect of the triazinane ligand on the reaction of enimines with metal complexes and the reactivity of the products of this reaction, we performed an experimental study of the reactions of (1,3,5-triorganyl-1,3,5-triazacyclohexane)tricarbonylmetals(0) with *N*-benzyl-(3-methylbut-2-enylidene)amine (α-enimine).